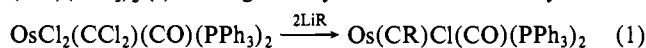


## An Osmium-Carbyne Complex

Sir:

Examples of terminal carbyne complexes, compounds with a formal metal-carbon triple bond, have been confined to transition metals from groups 5, 6, and 7 of the periodic table. Undoubtedly, this restricted occurrence is due to a lack of suitable synthetic approaches. These compounds result either from modification of alkoxycarbene complexes through reaction with boron trihalides<sup>1</sup> (which may involve the intermediacy of halocarbene species<sup>2</sup>) or from  $\alpha$ -H abstraction reactions on suitable ligands such as benzyl or neopentyl.<sup>3</sup> In one case, rearrangement of a molybdenum-vinyl compound led to a carbyne complex.<sup>4</sup> The availability of a dichlorocarbene complex of osmium,  $\text{OsCl}_2(\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$ ,<sup>5</sup> led us to explore the possibility of generating monochlorocarbene complexes (and hence carbyne species through rearrangement) through reaction of this  $\text{CCl}_2$  complex with lithium reagents. This approach turns out to be successful in leading to a carbyne complex, but a monochlorocarbene complex may not be an intermediate, and the detailed steps involved in the reaction are at present unclear. We describe here the synthesis and X-ray crystal structure determination of  $\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , reactions of this compound with the electrophiles  $\text{H}^+$  and  $\text{Cl}_2$  and with sulfur, selenium, and tellurium to yield novel carbene, chlorocarbene, thioacyl, selenoacyl, and telluroacyl derivatives, respectively.

Maximum yield of carbyne complex results when 2 equiv of lithium reagent are used (eq 1).<sup>6</sup> For  $\text{R} = p$ -tolyl,  $\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (I) forms green crystals obtained in 70% yield. IR



data for this and other compounds described herein are in Table I. Compounds with  $\text{R} = \text{C}_6\text{H}_5$ ,  $p$ - $\text{C}_6\text{H}_4\text{NMe}_2$ , and  $p$ - $\text{C}_6\text{H}_4\text{OMe}$  have also been obtained,<sup>8</sup> and similar ruthenium compounds are also being studied.<sup>9</sup>

The crystal structure determination<sup>10</sup> of I confirms the mononuclear formulation and reveals distorted trigonal bipyramidal geometry (see Figure 1) with the phosphine ligands mutually trans and the angle between  $\text{Os}-\text{Cl}$  and  $\text{Os}\equiv\text{CR}$  increased to  $133^\circ$ . The

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(6) We have no firm evidence for the steps involved in the reaction forming the carbyne complex. One possibility is that the lithium reagent first abstracts chlorine, forming a chlorocarbene intermediate,  $\text{Os}(\text{CCl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , which reacts further with  $\text{LiR}$  to yield  $\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ . The intermediacy of  $\text{OsCl}_2(\text{CClR})(\text{CO})(\text{PPh}_3)_2$  seems less likely since we have been unable to detect any carbyne complex from reaction of this compound with  $\text{LiR}$ . Experimental details for the preparation of  $\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  are as follows: a diethyl ether/hexane solution of  $p$ -tolyllithium (2.1 mol equiv) [prepared by heating under reflux  $n$ -butyllithium (23 mL of a 1 M solution in hexane) with  $p$ -bromotoluene (3.93 g) in diethyl ether (25 mL) for 0.3 h<sup>7</sup>] was rapidly added with vigorous stirring to a solution of  $\text{OsCl}_2(\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$  (5.00 g) (1 mol equiv) in benzene at  $20^\circ\text{C}$ . After 1 or 2 s, the reaction was quenched by pouring into  $n$ -hexane (1500 mL). The mixture was then set aside for 1.5 h, during which time dark green crystals separated from solution. Filtration followed by extensive washing with water, ethanol, and finally hexane (which removes impurities such as lithium chloride) yielded  $\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  ( $\text{R} = p$ -tolyl,  $\text{C} = \text{carbyne}$ ) (3.44 g, 70%). The product obtained by this method was of high purity, and recrystallization was not normally necessary. Analytically pure samples were obtained by recrystallization from dry dichloromethane/hexane solution containing diethylamine [ca. 0.02 mL per 0.10 g of  $\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ]. Anal. Calcd for  $\text{C}_{45}\text{H}_{37}\text{ClOOsP}_2$ :  $\text{C}$ , 61.32;  $\text{H}$ , 4.23. Found:  $\text{C}$ , 61.49;  $\text{H}$ , 4.55.

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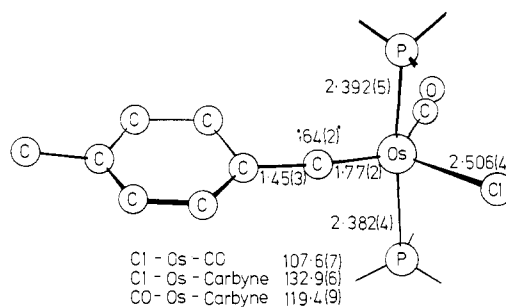
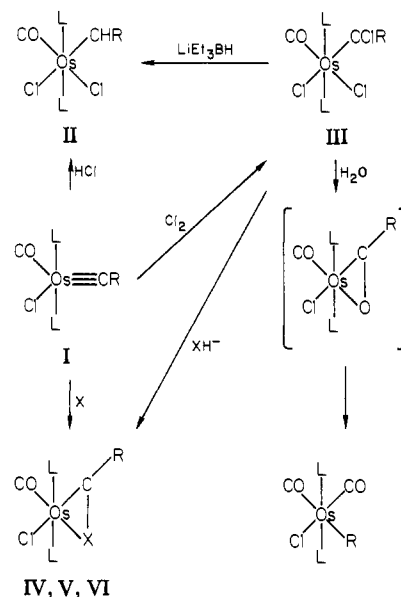
(9) Roper, W. R.; Wright, A. H., to be published.

(10) Crystal data and refinement results for  $\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ : monoclinic;  $a = 17.058$  (3),  $b = 12.792$  (1),  $c = 18.340$  (4) Å;  $\beta = 107.99$  (1)°; space group  $\text{P}2_1/n$ ;  $Z = 4$ . Intensity data were collected on a Nonius CAD-4 diffractometer, and the structure was solved by conventional heavy-atom methods. Full-matrix least-squares refinement has returned  $R = 0.040$  for 2216 observed reflections.

Table I. IR Data<sup>a</sup> for Osmium Complexes<sup>b</sup>

compd	$\nu(\text{CO})^c$	$\nu(\text{Os}-\text{Cl})$
$\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (I)	1864	266
$\text{OsCl}_2(\text{CHR})(\text{CO})(\text{PPh}_3)_2$ (II)	1967, 1950 <sup>d</sup>	281, 256
$\text{OsCl}_2(\text{CClR})(\text{CO})(\text{PPh}_3)_2$ (III)	1957	280, 257
$\text{Os}(\eta^2\text{-CSR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (IV)	1902	273
$\text{Os}(\eta^2\text{-CSeR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (V)	1927 (sh), 1911, 1899 (sh) <sup>d</sup>	270
$\text{Os}(\eta^2\text{-CTeR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (VI)	1932 (sh), 1914, 1902 (sh) <sup>d</sup>	270

<sup>a</sup> In reciprocal cm. Measured as Nujol mulls. <sup>b</sup> All compounds have satisfactory carbon and hydrogen analyses. <sup>c</sup> All bands very strong unless otherwise noted. <sup>d</sup> Solid-state splitting. II has  $\nu(\text{CO})$  1954 (vs) in  $\text{CH}_2\text{Cl}_2$ .

Figure 1. The inner coordination sphere of  $\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ .Scheme I. Reactions of  $\text{Os}(\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ <sup>a</sup>

<sup>a</sup>  $\text{R} = p$ -tolyl,  $\text{L} = \text{PPh}_3$ ,  $\text{X} = \text{S}$  (compound IV),  $\text{Se}$  (compound V), or  $\text{Te}$  (compound VI).

most conspicuous feature of the structure is the very short  $\text{Os}\equiv\text{CR}$  distance of 1.77 Å. In the IR spectrum, a medium to strong absorption at  $1359\text{ cm}^{-1}$  is tentatively assigned to  $\nu(\text{Os}\equiv\text{C})$  by analogy with the  $1315\text{-cm}^{-1}$  band assigned  $\nu(\text{W}\equiv\text{C})$  in  $\text{W}(\text{CCD}_3)_4$ .<sup>11</sup> This band disappears in all the compounds derived from I.

Although cationic carbyne complexes of manganese and ruthenium have been shown to react with nucleophiles, giving carbene complexes,<sup>12</sup> compounds with a metal-carbon triple bond might be expected to show reactivity toward electrophiles, and

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this is certainly true of the osmium-carbyne complex. I reacts with HCl, forming the osmium(II)-carbene complex  $\text{OsCl}_2\text{-(CHR)(CO)(PPh}_3)_2$  (II) (see Scheme I for a summary of this and other transformations described in this paper). The  $^1\text{H NMR}$  spectrum of II ( $\text{CDCl}_3$ ) shows a low-field resonance at  $\tau$ -8.05 [ $J(\text{P-H}) = 2.5$  Hz], a position typical of other alkylidene complexes.<sup>13</sup> However, unusual features of this compound are air stability, a mp of 255 °C, and a lack of further reactivity with HCl. Reaction of I with  $\text{Cl}_2$  leads to a 1:1 addition product which we formulate as the osmium(II)-chlorocarbene complex  $\text{OsCl}_2\text{-(CClR)(CO)(PPh}_3)_2$  (III). Further reactions of III support this formulation. As detailed in Scheme I, 1 equiv of  $\text{Li(Et}_3\text{BH)}$  converts III to II; reaction with water leads to the osmium *p*-tolyl dicarbonyl  $\text{OsRCl(CO)}_2\text{(PPh}_3)_2$ , easily understood as resulting from an intermediate acyl complex,<sup>14</sup> and reaction with  $\text{SH}^-$  produces the known  $\eta^2$ -thioacyl IV.<sup>15</sup> Similarly, reaction with  $\text{SeH}^-$  and  $\text{TeH}^-$  leads to examples of previously unknown  $\eta^2$ -selenoacyl and  $\eta^2$ -telluroacyl ligands, respectively. If the osmium-carbon triple bond is thought of as having "acetylene-like" character, then the thioacyl derivative can be thought of as an unsaturated episulfide derived from the carbyne complex. We therefore attempted the synthesis of the thioacyl directly from I and elemental sulfur and found that this reaction proceeds virtually quantitatively in benzene solution at room temperature over several minutes. Similar reactions with elemental selenium and tellurium are much slower but nevertheless proceed in good yield. Other reactions of I are suggested by the acetylene analogy and will be described subsequently.

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George R. Clark, Karen Marsden, Warren R. Roper\*  
 L. James Wright  
 Department of Chemistry, University of Auckland  
 Auckland, New Zealand  
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### 1:14 Heteropolyvanadate of Phosphorus: Preparation and Structure

Sir:

A variety of heteropolyanions of vanadium have been reported but with few confirmed examples of structure determination.<sup>1</sup> In the case of phosphorus as the heteroatom, the knowledge about compositions and structures of heteropolyvanadates is still limited. There have been several reports of the preparation of  $\text{PV}_{12}\text{O}_{36}^{7-}$ ,<sup>2</sup> but the existence of this anion was doubted by Preuss and Schug. Instead, they claimed to have characterized 1:13 and 1:14 vanadophosphates by chemical analyses and the ultracentrifuge technique.<sup>3</sup> We report here the isolation of 1:14 vanadophosphate as a guanidinium salt crystal suitable for X-ray characterization which revealed a new structural type, a bicapped Keggin structure.

- (1) The structures of  $\text{Ni}(\text{IV})\text{V}_{13}\text{O}_{38}^{7-}$ ,  $\text{Mn}(\text{IV})\text{V}_{13}\text{O}_{38}^{7-}$ , and  $\text{AlV}(\text{V})_{12}\text{V}(\text{IV})_2\text{O}_{40}^{9-}$  which have octahedrally coordinated heteroatoms were established. C. M. Flynn, Jr., and M. T. Pope, *J. Am. Chem. Soc.*, **92**, 85 (1970); A. Kobayashi and Y. Sasaki, *Chem. Lett.*, 1123 (1975); H. T. Evans, Jr., and J. A. Konner, *Am. Mineral.*, **63**, 863 (1978). The only known example of heteropolyvanadates containing tetrahedrally coordinated heteroatoms was  $\text{H}_6\text{As}_6\text{V}_4\text{O}_{30}^{4-}$ : A. Durif and M. T. Averbuch-Pouchot, *Acta Crystallogr., Sect. B*, **B35**, 1441 (1979).  
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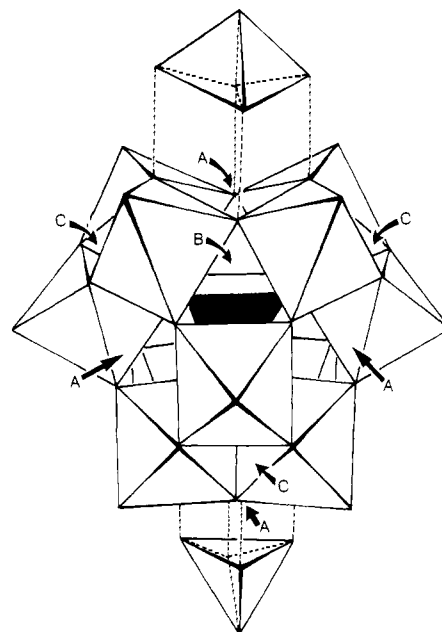


Figure 1. The polyhedral model of the  $\text{PV}_{14}\text{O}_{42}^{9-}$  anion.

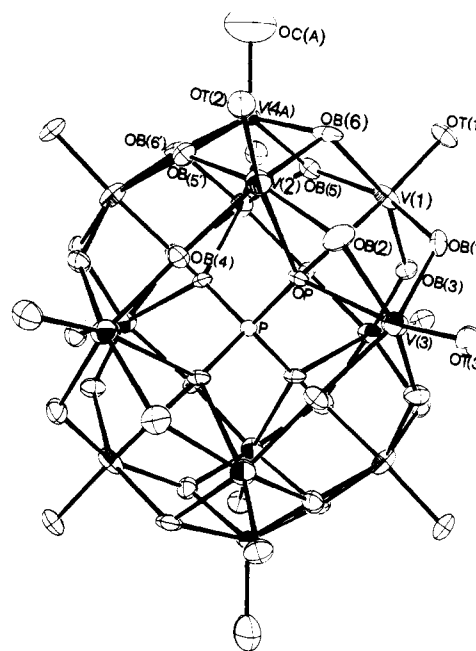


Figure 2. The geometry of the  $\text{PV}_{14}\text{O}_{42}^{9-}$  anion. Bond lengths: P-OP, 1.529 (5); V(1)-OT(1), 1.608 (6); V(1)-OB(1), 1.831 (6); V(1)-OB(3), 1.891 (5); V(1)-OB(5), 1.981 (5); V(1)-OB(6), 1.922 (6); V(1)-OP, 2.350 (5); V(4A)-OC(A), 1.681 (10); V(4A)-OB(5), 1.829 (6); V(4A)-OB(6), 1.999 (6) Å. Bond angles: OC(A)-V(4A)-OB(5), 116.4 (4); OC(A)-V(4A)-OB(6), 103.3 (4)°.

An insoluble dark red solid was obtained by treating an aqueous solution of  $\text{H}_3\text{PO}_4$  and  $\text{NaVO}_3$  (ref 4, 1:4 ratio, pH 2.7 with  $\text{HNO}_3$ )<sup>4</sup> with excess guanidine hydrochloride in water at room temperature. An octahedral single crystal for X-ray investigation was prepared by a diffusion method. Anal. Calcd for  $(\text{CN}_3\text{H}_6)_8\text{H(PV}_{14}\text{O}_{42})\cdot 7\text{H}_2\text{O}$ : C, 4.75; H, 3.14; N, 16.61; V, 35.2; P, 1.53. Found: C, 4.86; H, 3.28; N, 16.64; V, 35.3; P, 1.44. The IR spectrum was similar to those of  $\text{PM}_{12}\text{O}_{40}^{3-}$  ( $M = \text{Mo, W}$ ) having the Keggin structure.

Crystal data for  $(\text{CN}_3\text{H}_6)_8\text{H(PV}_{14}\text{O}_{42})\cdot 7\text{H}_2\text{O}$  ( $M_w$  2024.08): tetragonal, space group  $I\bar{4}$ ;  $a = 13.058$  (2),  $c = 18.431$  (6) Å;  $U = 3143$  (1) Å<sup>3</sup>;  $Z = 2$ ;  $d_{\text{calcd}} = 2.14$  g cm<sup>-3</sup>;  $\mu(\text{Mo K}\alpha) = 22.5$  cm<sup>-1</sup>. The structure was solved by the heavy-atom method and

(4) Ca. 0.2 M in  $\text{H}_3\text{PO}_4$ .